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THE CHEMISTRY OF CHLORAMINES

By J. F. T. Berliner[1]

In the term "chloramine" the chemist includes all amino ($-NH_2$) or imino ($=NH$) groups in which the hydrogen has all or in part been replaced by chlorine. The term "chloramine" to those in the medical and pharmaceutical professions refers more or less specifically to the mono- and di-chlorine substituted toluine sulphonamide derivatives, usually known as Chloramine-T, Halazone or Dichloramine-T. To those interested in the treatment of water and related endeavors the term is restricted to the chlorine substitution products of ammonia. Even in this field the term "chloramine" has come, through general usage, to indicate monochloramine, NH_2Cl. However, in almost every application of chloramines to water treatment we are dealing with a variable mixture of the mono- and di-chloramine ($NHCl_2$). Under certain extreme conditions the trichloramine or nitrogen trichloride (NCl_3) can be formed in the treatment of water, but it is seldom encountered and is decidedly undesirable.

Chloramines are produced in water by the introduction of ammonia and chlorine. The process is not new. It was first proposed about 1904. Interest in its possibilities has been dormant for more than a score of years. In fact, widespread interest and application of the ammonia-chlorine treatment to municipal and private water supplies began just about one year ago. On January 1, 1930, there were but about five installations in the United States employing this process. By September 1, 1930, this number had increased to 70 and on May 25, 1931, the recorded number of installations is 190.

This remarkable and sudden development has centered considerable interest on the basic chemistry of the process. It has, therefore, been considered timely to summarize briefly the available information on the nature and properties of chloramines, their reactions and interrelations, and to assemble for reference citations to the more important studies on these phases.

The existence of chloramines had been noted as early as 1811 by

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P. L. Dulong (1), who first recorded the preparation of the explosive trichloramine and, as Mellor (2) states, continued to work on it after it had caused him the loss of three fingers and one eye.

A voluminous amount of investigation and study has been reported on the properties and reactions of trichloramine, and of the three chloramines this is by far the most completely known. Unfortunately this chloramine is of the least significance or interest to the members of the water works profession. Because of its relative unimportance little space will be devoted to it. However, it may be of value to note that two excellent summaries of the literature on the properties and preparation of trichloramine exist, one supplied by Mellor (2) (see ref. No. 1, page 611) and the other by Gmelin (3). The latter is somewhat more complete.

Very little has been published on the physical and chemical properties of the pure mono- and di-chloramines. In fact, practically nothing is known of the properties of dichloramine except that as regards odor, volatility, partial pressure in solution, etc.; they are intermediate between those of mono- and tri-chloramine.

It may be of interest to first examine the physical and chemical properties of the pure chloramines and then to consider their reactions, properties and interrelation in aqueous solutions.

PHYSICAL PROPERTIES AND PREPARATION OF PURE CHLORAMINES

The chloramines when pure are all rather oily, extremely unstable liquids with an acrid odor. They are all water-soluble. The trichloramine is, however, but slightly soluble in water. The solubilities of the three chloramines in various organic solvents vary considerably. This property affords a means for their separation. For instance, monochloramine is practically insoluble in carbon tetrachloride, the dichloramine is soluble to a small extent and the trichloramine is very soluble in this solvent. Monochloramine is but slightly soluble in ethyl ether but the dichloramine is highly soluble in this material.

The three chloramines may be formed under varying conditions through reaction between chlorine or hypochlorous acid or its derivatives and ammonia or certain ammonium salts. The usual method of obtaining the pure chloramines is to first prepare them in the form of a strong aqueous solution and then extract these solutions with suitable organic solvents or to distil the chloramine from the aqueous solution by vacuum treatment or gas washing.

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Monochloramine

Because of the ease of decomposition in its pure free state, little is known of the physical properties of monochloramine.

It is an oily colorless liquid, which on cooling solidifies to an amorphous glassy mass and under certain conditions, in part takes on a white crystalline form. It has, when concentrated a somewhat acrid pungent odor (24, 26, 27) lying between that of ammonia and trichloramine (4). The melting point of monochloramine is reported as −66°C. If ammonia is present as an impurity, the melting point is reduced 3 or 4°C. At −65°C. the liquid has a very low vapor pressure. However, at about −50°C. violent and at times explosive decomposition occurs. This decomposition yields nitrogen, chlorine, and a voluminous mass of yellow oily droplets of trichloramine interspersed with white crystalline ammonium chloride (4).

Monochloramine is about as soluble in water as ammonia. It is but slightly soluble in benzol, chloroform and carbon tetrachloride, though readily soluble in ethanol and ether. The partition ratio between water and ether with a fresh solution (4) is about 1:0.97. On standing, some monochloramine is converted to trichloramine and this is completely absorbed from the ether layer. The partition ratio of monochloramine between water and chloroform is 1:0.25 (5).

When a concentrated aqueous solution of monochloramine is maintained at a low temperature it deposits yellow crystals of chlorine hydrate. At 0°C. decomposition with formation of nitrogen soon commences (4). The decomposition increases at an accelerated rate because of the catalytic action of the liberated acid. The presence of a very small amount of ammonia greatly stabilizes (4) the aqueous solution and there is evidence that one of the fundamental requirements for the formation of chloramine is a decided excess of ammonium ions (30).

Monochloramine is prepared by washing a relatively concentrated chloramine solution with benzol, chloroform or carbon tetrachloride to remove the tri- and di-chloramine. A slight excess of ammonia is then added to stabilize the monochloramine and the solution distilled in a vacuum employing a drying agent such as soda-lime and rapidly condensing the resultant vapors with liquid air or similar refrigerants. The excess ammonia is removed by vacuum treatment of the refrigerated condensate (4).

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Dichloramine

Practically nothing is known regarding the physical properties of dichloramine, except that, as stated before, they are intermediate between those of mono- and tri-chloramine. Its existence was probably first noted by Gatterman (8).

The following partition ratios for dichloramine in water have been reported; to chloroform 1:1.88; to carbon tetrachloride 1:0.85; to ether 1:47.3 (5). Dichloramine may be obtained by preparing a chloramine solution under such conditions of acidity that only the dichloramine and some trichloramine may be present. The trichloramine is removed as in the preparation of monochloramine. The dichloramine can then be concentrated by extraction with ethyl ether.

Trichloramine

The physical properties of trichloramine or nitrogen trichloride have been determined to some degree of completeness. Its boiling point is reported as +71°C. It is still liquid at −40°C. Its density is about 1.6. Trichloramine is only slightly soluble in water but readily soluble in benzol, carbon bisulphide, chloroform, ether, ethanol, carbon tetra-chloride, sulphur dichloride and phosphorus trichloride.

Trichloramine is a yellow, thick oily liquid with a pungent odor resembling chlorine. The liquid is stated to be a non-conductor of electricity (7). It is an explosive compound which detonates spontaneously, especially in the presence of organic matter. It explodes with a bright flash and a loud report and has a violent detonating wave. It is very liable to spontaneous decomposition and extreme care should be employed in handling. It can be detonated by exposure to magnesium light or direct sunlight (8) and mere contact with many substances causes rapid decomposition.

Trichloramine can be directly formed through mixing together the proper proportion of anhydrous solutions of ammonia and chlorine in chloroform or pentane cooled to −90°C. or lower ($4NH_3 + 3Cl_2 = 3NH_4Cl + NCl_3$). The by-product, ammonium chloride, precipitates out and the trichloramine can be separated from the solvent by vacuum distillation. Trichloramine may also be formed by passing air or other gas through an aqueous solution containing trichloramine and absorbing the trichloramine carried over by the gas in a suitable solvent. A number of interesting methods for the preparation

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of the trichloramine have been devised and are well summarized in the treatises of Gmelin (3) and of Mellor (2).

CHEMICAL PROPERTIES OF THE CHLORAMINES

The preparation of the aqueous solutions of the three chloramines involves two essentials, namely: The proper proportions of ammonia to chlorine and the proper control of the acidity or hydrogen-ion concentration of the solution. Before considering this phase of the subject, the general chemical properties of the chloramines should be considered. Monochloramine is the most important from our viewpoint and will be considered first and in most detail.

Monochloramine

It is well known that when aniline is treated with chlorine or hypochlorite solution, a blue-violet coloration is obtained. However, if ammonia is present prior to the addition of the chlorine, no coloration is produced (23). Similarly, the presence of ammonia prevents the usual reaction between phenol and chlorine. Mixing concentrated solutions of ammonia and of sodium hypochlorite causes an immediate evolution of nitrogen and the formation of some nitrates and other nitrogen oxidation products. If the solutions are diluted before mixing, nitrogen will only be evolved, if at all (15), after a considerable period of time. Departure from the relation $2NH_3 + 3Cl_2 = HCl + N_2$ appears to increase with dilution. These and other factors led investigators to the conclusion that compounds intermediate between ammonia and nitrogen were being formed. These compounds are the chloramines and under general conditions predominantly monochloramine.

The formation of monochloramine through the action of chlorine, hypochlorous acid or a hypochlorite on ammonia is considered to be preceded by the intermediate formation of ammonium hypochlorite,

$$Cl_2 + H_2O = HOCl + HCl$$
$$HOCl + NH_3 = NH_4OCl$$

Ammonium hypochlorite is very unstable and is rapidly transformed into monochloramine and water (28)

$$NH_4OCl = NH_2Cl + H_2O$$

In this reaction some traces of nitrous oxide have been evidenced (32, 6) in relatively concentrated solution. The formation of

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nitrites and nitrates through oxidative action on dilute chloramine solutions has also been noted (2, 33, 6).

Chapin has concluded (6) that elementary chlorine is inert towards ammonium ions, requiring conversion to hypochlorous acid before the reaction occurs.

Braidech (33) has recently made the interesting suggestion that a buffering or stabilizing action may result from the formation of complex molecular aggregates of the hydrates of ammonia and chlorine, in equilibrium with the associated molecules which compose the intramolecular structure of water at ordinary temperatures.

Monochloramine reacts neutral in water. In aqueous solution it tends to decompose at a rate commensurate with the concentration (under equivalent temperature conditions) into nitrogen, ammonium chloride and hydrochloric acid (10),

$$3NH_2Cl = N_2 + NH_4Cl + 2HCl$$

This reaction is rapidly accelerated by catalysts such as sponge platinum (4) or acids (33).

In very concentrated aqueous solutions (of the order of about 10 per cent, the presence of trichloramine has been noted (4) in its decomposition products.

Raschig (13) has recorded the decomposition reaction for concentrated monochloramine solutions to be

$$4NH_2Cl = 2NH_4Cl + N_2 + Cl_2$$

The tendency has been reported for the formation of hypochlorous acid through the hydrolytic reaction

$$NH_2Cl + H_2O = NH_3 + HClO$$

which may occur under certain conditions (24).

Monochloramine is decomposed by concentrated hydrochloric acid according to the reaction (31)

$$NH_2Cl + 2HCl = NH_4Cl + Cl_2$$

The reaction with hydriodic acid is similar (10). Diluted hydrochloric acid yields condition for the formation, through successive stages, of trichloramine,

$$3NH_2Cl + 2HCl = NCl_3 + 2NH_4Cl$$

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The acidification of monochloramine involves the formation of dichloramine which is considered to progress in two steps (6),

$$NH_2Cl + HCl + H_2O = NH_4Cl + HClO$$
$$NH_2Cl + HClO = NHCl_2 + H_2O$$

The conversion of di- to tri-chloramine probably involves analogous steps.

It has been considered more or less typical for the chloramines to decompose or rearrange themselves in such a manner as to re-form ammonia or ammonium salts. There is the opposing tendency for the more complete decomposition to elemental nitrogen. Both of these reactions manifest themselves in the alkaline decomposition of monochloramine (12),

$$3NH_2Cl + 3KOH = NH_3 + N_2 + 3KCl + 3H_2O$$

or (13)

$$3NH_2Cl + 2NaOH = NH_4Cl + N_2 + 2NaCl + 2H_2O$$

More recent considerations (6), however, indicate that the alkaline treatment of monochloramine may lead to the formation of hypochlorites.

When an attempt is made to prepare concentrated chloramine solutions by treating ammonia solutions with sodium or calcium hypochlorite, chloramine is formed in the presence of relatively high concentrations of alkali ($NH_3 + NaOCl = NH_2Cl + NaOH$). The chloramine that is formed tends to be immediately decomposed by the alkali to yield nitrogen and ammonia according to the above reactions. The final result of the reaction between concentrated ammonia and an alkaline hypochlorite solution is, therefore,

$$2NH_3 + 3NaOCl = 3NaCl + 3H_2O + N_2$$

There is also the contemporary side reaction involving the intermediate formation of ammonia and alkali to form hydrazine (13),

$$NH_2Cl + NH_3 + NaOH = N_2H_4 + NaCl + H_2O$$

Another side reaction that ensues is the formation of chlorate,

$$3NH_2Cl + 3NaOH = 3NH_3 + KCl + KClO_3$$

Marckwald and Wille mixed equal volumes of 0.1 N monochloramine solution and 0.25 N potassium hydroxide solution and noted the for-

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mation of nitrogen according to the reactions previously given. When the reaction had been completed through warming, about 12.5 percent of the chlorine in the original chloramine was found combined in the form of chlorate.

Another side reaction has been noted by Thiele (15) which indicates the formation of hydroxylamine (NH_2OH). This involves further reaction between hydroxylamine and hydrazine to form ammonia, nitrogen and water. The presence of hydrazoic acid (N_3H) has also been noted in the products of the alkaline decomposition of monochloramine (22).

Chloramine reacts towards ammonia essentially as with the alkali hydroxides, thus:

$$3NH_2Cl + 2NH_3 = N_2 + 3NH_4Cl$$

In studying this reaction Thiele (15) was the first to note the presence of a small amount of a strong reducing substance. Although he did not identify the material it was later recognized to be hydrazine,

$$NH_2Cl + NH_3 = N_2H_4 + HCl \quad (22)$$

This method for the production of hydrazine has been the subject of some investigation and it has been found that substances that increase the viscosity of a solution, such as glycerine, sugar, albumin, casein, etc., act as catalysts towards the formation of hydrazine. Raschig (12, 13, 14) claims an 80 percent conversion.

It should here be emphasized that the above reactions refer almost entirely to relatively concentrated solutions. In somewhat dilute solutions, ammonia acts as a powerful stabilizer for chloramine and prevents its decomposition or reversion to nitrogen, ammonium chloride, ammonia, hydrazine, hydrochloric or hypochlorous acid, hydroxyl amine, chlorates, hydrazoic acid, chlorine or the other chloramines. Dilute chloramine solutions in the presence of an excess of ammonia may be distilled without decomposition (4).

The formation of hydrazine through the reaction between ammonia and monochloramine is not of importance in the treatment of water, as there is no evidence that this reaction will take place in dilute solution of chloramine. Solutions containing about 150 parts per million chlorine and 250 percent excess ammonia will not develop a detectable trace of hydrazine.

There are a number of other reactions of interest but only those of

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more immediate importance have been considered. Chloramine reacts with hypochlorite to form trichloramine (4),

$$NH_2Cl + 3NaOCl = NCl_3 + 2NaOH$$

Sulphites or bisulphites reduce chloramine solutions (1)

$$NH_2Cl + SO_2 + H_2O = NH_4 \cdot HSO_4 + HCl$$

However, a series of side reactions involve the formation of amido sulphonic acid derivatives (13),

$$NH_2Cl + Na_2SO_3 = NH_2SO_3Na + NaCl$$

When a solution of monochloramine is treated with a solution of a silver salt, the solution remains clear at first then gradually silver chloride is precipitated (3). If a neutral or ammoniacal solution of silver salt be employed, metallic silver will be deposited slowly (29, 13).

Dichloramine

Dichloramine is a close second to monochloramine in importance in water treatment and deserves as much consideration. Unfortunately very little is known of the chemical properties of this substance. However, it may be judged that in many respects its behavior will be analogous to that of monochloramine.

Like monochloramine it will liberate iodine in a starch-iodide solution. On treatment with concentrated ammonia solution, decomposition ensues according to the reaction (13)

$$3NHCl_2 + 7NH_3 = NH_4Cl + 2N_2$$

The acidification of dichloramine leads to the formation of trichloramine while the treatment of a dilute solution of dichloramine with alkali forms some monochloramine and involves a number of reactions, the principal one appearing to be the formation of hypochlorites (6) thus

$$NHCl_2 + 4NaOH = 3NaCl + NaOCl + 3H_2O + N_2$$

The presence of oxidation products of nitrogen such as nitrites also have been noted.

Trichloramine

The chemical properties of trichloramine, the chloramine of least interest in water treatment, are better known than those of the other chloramines.

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Trichloramine in non-aqueous solutions decomposes, at a rate depending on the temperature and concentration, to nitrogen and chlorine (16),

$$2NCl_3 = N_2 + 3Cl_2$$

In aqueous solutions this reaction may also take place to a small extent, but the principal reaction appears to be, especially under acid conditions, the formation of hypochlorous acid according to the equation (17)

$$NCl_3 + 3H_2O = NH_3 + 3HClO$$

This reaction had led to the hypothesis that trichloramine is an amido anhydride of hypochlorous acid, since this acid and not hydrochloric acid is formed on hydrolysis (18). This view readily explains the ease of the reaction

$$NCl_3 + 4HCl = NH_4Cl + 3Cl_2$$

For further discussion of this point the works of Noyes (19) should be consulted.

Trichloramine reacts with an excess of ammonia to yield nitrogen or ammonium hypochlorite (24),

$$NCl_3 + 4NH_3 = NH_4Cl + N_2$$
$$NCl_3 + 2NH_3 + 3H_2O = 3NH_4OCl$$
$$NH_4OCl = NH_2Cl + H_2O$$

The treatment of nitrogen trichloride with alkali leads as with dichloramine to the formation of hypochlorites (6)

$$2NCl_3 + 6NaOH = 3NaCl + 3NaOCl + 3H_2O$$

A number of side reactions are also involved, one of which results in the formation of nitrites.

Trichloramine in solution can be reduced to ammonia by such substances as sodium sulphite (21). Silver nitrate solutions deposit silver chloride on treatment with trichloramine (20).

It should be recorded that Porret (7) claims that below 0°C. no trichloramine could be formed and that temperatures above 32°C. are most favorable for its formation. He further claimed that sulphur, ammonium sulphide, powdered charcoal or dilution of the chlorine with 1/3 to 1/2 with air CO_2 or hydrogen inhibited the

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formation of trichloramine. These claims have not been substantiated and to some extent have been refuted by subsequent evidence.

Bray and Dowell (21) concluded that the reaction depended primarily on the acidity of the solution and showed that in the presence of strong acids ammonia and chlorine reacted to form trichloramine, thus

$$NH_3 + 3Cl_2 = NCl_3 + 3HCl$$

In strongly basic solutions nitrogen is formed, thus

$$8NH_3 + 3Cl_2 = N_2 + 6NH_4Cl$$

They considered these reactions to be a series of consecutive reactions (19), the first of which is the formation of monochloramine,

$$2NH_3 + Cl_2 = NH_2Cl + NH_4Cl$$

INTERRELATION OF CHLORAMINES

In the average treatment of water with ammonia and chlorine the two most predominant reactions between the ammonia and chlorine are

$$2NH_3 + Cl_2 = NH_2Cl + NH_4Cl \text{ (A)}$$

and

$$3NH_3 + 2Cl_2 = NHCl_2 + 2NH_4Cl \text{ (B)}$$

The relative proportion of mono- and di-chloramine formed, is governed principally by the final hydrogen ion concentration of the solution. Under average conditions the monochloramine reaction (A) predominates. This reaction requires theoretically one part of ammonia to two of chlorine (1:2). However, there is evidence indicating that an excess of ammonia or rather ammonium ions in solution is a requirement for chloramine formation (30, 5, 6). It has been established that the presence of an excess of ammonium ions, under proper conditions of hydrogen ion concentration, acts as a very active stabilizer in preventing the decomposition of monochloramine. The practical aspect of this is illustrated in the great number of installations that through numerous trials have found an optimum ratio of two parts of ammonia to three parts of chlorine (2:3).

The conditions which limit the formation of the three chloramines in aqueous solutions were not until very recently quite understood.

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Bray and Dowell (21) state: "The reactions between chlorine and ammonia in aqueous solution furnish striking examples of changes in the nature of the product which result from variations in experimental conditions."

It has long been recognized in the reaction of ammonia and chlorine in solution that acidity leads to the formation of nitrogen trichloride and alkalinity towards monochloramine. Chapin has carefully studied the formation and transformation of the chloramines and has determined the ranges of hydrogen ion concentration limiting the existence of the three chloramines.

The concentration of hydrogen ions in the medium in which the reaction occurs is the only governing factor providing the reacting materials are rapidly mixed, sufficiently buffered and cooled, and there is an excess of ammonium ions (5). Chapin demonstrated that under these conditions, above a pH of 8.5, only monochloramine could be formed; in the range 4.4 to 5.0 dichloramine was formed and trichloramine could only be formed below pH of 4.4. Between the pH range 5.0 to 8.5 mono- and di-chloramine coexist in a ratio fixed by the hydrogen ion concentration of the solution. At neutrality (pH = 7) there are approximately equal amounts of mono- and dichloramine present. Acidification of a monochloramine solution causes a gradual, proportional conversion to the dichloramine or trichloramine, or finally to nitrogen on storage.

$$2NH_2Cl + HCl = NHCl_2 + NH_4Cl$$
$$3NHCl_2 + HCl = 2NCl_3 + NH_4Cl$$

It should be pointed out that there is a factor of time involved in the conversion of one chloramine to another by control of the hydrogen ion concentration. These reactions are not completely reversible for when solutions of dichloramine and of trichloramine are treated with alkali there is a tendency for side reaction to occur, involving the loss of nitrogen and the formation of chlorides and hypochlorites. The extent of these side reactions is governed principally by the concentration of the reactants and the acidity and temperature of the solution.

From these considerations it is apparent that in the preparation of chloramine solutions it is essential that the acidity of the medium in which the reaction occurs be controlled before and during the progress of the reaction. In many instances attempts have been made and instructions have been published to prepare chloramine

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solutions by passing ammonia into an aqueous solution of chlorine. If this chlorine solution is acid, as it may be unless sufficient alkali has been added or was originally present, different products than originally desired may be formed. For instance, the addition of ammonia to a solution of chlorine with an acidity of about pH 3 will at first lead to the formation of trichloramine and some products of side reactions. As the addition of the ammonia continues, the solution becomes progressively more alkaline and dichloramine and finally monochloramine are produced. The final concentration of chloramine will be considerably less than that which could be produced by the addition of the equivalent amount of chlorine to the same quantity of ammonia in solution.

In this inclusive subject of the chemistry of chloramines it is apparent that we are dealing with three compounds that can undergo numerous involved reactions and that are very closely interrelated. They exhibit unusual physical and chemical properties which are highly dependent on their state of concentration. A complete separate chemistry could be written for these compounds in various degrees of concentration. The aqueous solutions with a maximum concentration of about 0.0001 per cent (1.0 p.p.m.) are of most importance to those interested in water treatment. We have by allowable analogy a fair understanding of the chemistry of the chloramines at these concentrations. We do not have for these conditions as complete a knowledge as desirable of the rates of reaction and conversion, the effects of mass action of the reactants, or the influence of sulphates, carbonates and other such materials as are found or are added to water under treatment.

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